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### Laser markable polymeric compositions

The present invention relates to improved polymeric compositions having laser-marking properties.

The marking of, and printing onto, polymeric materials in an indelible fashion is required in many different applications. Domestic articles, engine parts for automobiles, key tops for computer keyboards and other similar products are often marked with letters, symbols or other markings. Such markings can be applied by using a curable ink. However, there are usually high production costs involved in using curable inks as there are a number of separate steps required for the application and curing of such inks.

An alternative is laser marking. In laser marking a laser is used in conjunction with a polymeric material which has incorporated therein a suitable laser marking compound. The wavelength of the laser beam is tuned according to the compound to cause the polymeric material to burn resulting in a clear contrast between the irradiated area and the rest of the product.

An example is EP-A-0 867 466 which teaches a polyolefin resin composition comprising 100 parts by weight of a polyolefin resin and 0.01 to 20 parts by weight of a black pigment mainly comprising a metal oxide. When a laser beam is applied to the resin, the black pigment decomposes in the irradiated areas and is completely released. As a result, lighter coloured markings are obtained in contrast to the unmarked area of the moulded article, which is black.

However, in many circumstances it is desirable to mark a polymeric product which is brightly coloured. The polyester resin composition of EP-A-0 867 466 is capable of only providing white barcode markings against a black background and therefore is not useful if the background area is a lighter colour.

JP-A-2001/071 645 describes a resin composition comprising a thermoplastic resin, a sulphide and pigments including coloured pigments and a black stain pigment –

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in particular carbon black having a mean particle size of 10 to 90 nm. When a laser beam of wavelength from 354 nm to 1064 nm is applied to the resin, the carbon black absorbs the laser beam, converts it into heat energy and a marking with a "very high degree of black" is obtained. This prior patent specification describes the use of laser marking to produce a black barcode. This barcode is said to contrast with the non-irradiated area of the moulded article. However, it has been found that the composition described in JP-A-2001/071 645 does not work well where the background is a bright colour such as pink or yellow.

One particular area where coloured resins are used is for the production of livestock items such as ear tags. Ear tags are traditionally used by farmers as a means of tracking and readily identifying stock. Tags are typically made of thermoplastic resins and are marked with letters, digits, patterns, barcodes, pointcodes or symbols, including also purely decorative designs and trademarks. It is often desirable to use tags or sets of tags of bright, optionally different, colours (and if desired different forms). In the context of, for example, handling livestock, the use of colours such as yellow or pink enables handlers to readily segregate and group livestock. There is a need in this application, and of course many other applications, where the laser marking of brightly coloured polymeric compositions is desirable. Accordingly, it is an object of the present invention to provide an improved polymeric composition which enables a laser marking process to be used to produce dark marking particularly where the polymeric composition is brightly coloured.

In one aspect of the present invention there is provided a composition having laser-marking properties, said composition comprising a polymeric material, mica or a micaceous material and a metal sulphide.

Surprisingly it has been found that when a laser beam is applied to the surface of an article formed from such a polymeric composition prominent, clearly defined and sharp dark marking is achieved in the irradiated areas even when the polymeric resin is brightly coloured. More particularly, it is possible when using the compositions of the present invention to produce fine and well resolved dark

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marking so that detailed graphics such as bar-codes can be marked onto polymeric products whether these products are white or some other colour. Whilst mica and micaceous materials have been used in the past for laser marking of polymeric materials, the applicants have surprisingly found that the addition of a metal sulphide will significantly improve the quality of the marking. The use of a metal sulphide alone does not give rise to dark marking when irradiated by laser and the synergistic effect was unexpected.

In a second aspect of the present invention there is provided an article; said article being formed from a composition which comprises a polymeric material, mica or a micaceous material, and a metal sulphide; wherein the article so formed is adapted to exhibit dark markings in areas irradiated with a laser beam.

In a third aspect of the present invention there is provided a method of producing an article having laser marked surface portions, said method comprising:

- (a) providing a polymeric material;
- (b) compounding said polymeric material with mica or a micaceous material and a metal sulphide to provide a polymeric composition;
- (c) forming an article using the polymeric composition; and
- (d) irradiating said article with a laser beam to produce laser marked surface portions on the article.

As used herein, the term "marking" refers to any laser mark whatsoever and is not limited to letters. It includes the application of patterns, barcodes, symbols or drawings and the like.

The polymeric material used in the present invention is not particularly limited and may be selected from a wide range of resins including polyolefins, polyurethanes, polycarbonates, polyesters, rubber modified monovinylidene, aromatic resins, polyetherimides, polyamides, polyimides, polyester carbonates, polyphenylene sulphides, polyamideimides, polyesteramides, polyether esters, polyetherimide esters, polyarylates, polymethylpentenes, polysulfones, polyethersulfones,

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polystyrenes, rubber modified high impact polystyrenes, polyoxymethylenes, styrene maleic anhydride copolymers, acrylonitrile styrene acrylate copolymers, acrylonitrile butadiene styrene copolymers (ABS), polyphenylene ethers, polyether ketones, chlorinated polymers, fluorinated polymers, and liquid crystal polymers. In  
5 a more preferred aspect the polymeric material is selected from the group consisting of polyurethanes, polyamides, ABS, polycarbonates and rubber modified monovinylidene aromatic resins and blends thereof. Most preferred is a thermoplastic polyurethane resin.

The mica or micaceous material used in the present invention may be any such  
10 material which when combined with a polymeric resin and irradiated with a laser beam will cause dark marking. Natural or synthetic micas can be utilized. Preferably the mica or micaceous material is treated or doped with one or more metal compounds. The metal compounds may be present as one or more thin, coloured or colorless layers on the surface of the mica or micaceous material, or in  
15 discontinuous areas, too. Each such layer or array of discontinuous areas may be light-interfering or non-light-interfering. Preferably the metal compounds comprise, preferably consist of one or more metal oxides, e.g. such as oxides of antimony and/or titanium and/or tin, or oxides of iron and/or aluminium and/or silicium. Alternatively mica or micaceous materials coated or treated with bismuth  
20 oxychloride may be utilized. The mica or micaceous material preferably has a density of between 2.8 to 4.0 g/cm<sup>3</sup>. Preferably it has a Mohs hardness of 2.5 to 4 and oil absorption values of 35 to 70.0 grams per 100 grams of powder. Preferably the amount of mica ranges from 0.05 to 2 percent by weight based on the total weight of the composition. More preferably, the amount of mica present is from  
25 about 0.1 to about 0.5 percent by weight, based on the total weight of the composition.

The metal sulphide can be the sulphide of any metal with any known stoichiometry, such as MeS, MeS<sub>2</sub>, Me<sub>2</sub>S<sub>3</sub> or Me<sub>3</sub>S<sub>4</sub>, wherein Me is a metal of group 1-14 of the periodic system, especially a transition metal of group 9-12 of the periodic system,  
30 for example cadmium(II) sulphide, cobalt(II) sulphide, cobalt(II,III) sulphide

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(linneit), cobalt(III) sulphide, cobalt(IV) sulphide (cattierite), copper(I) sulphide (chalkosite), copper(II) sulphide (covellin), iron(II) sulphide, iron(III) sulphide, iron(IV) sulphide (pyrite, markasite), nickel(II) sulphide (millerite) or zinc(II) sulphide. Mixed sulphides of two or more metals are also suitable. The metal  
5 sulphide may contain other components, such as impurities or crystal water.

The metal sulphide is desirably selected from the group consisting of cadmium sulphide, iron sulphide, zinc sulphide and mixed sulphides comprising cadmium, iron or zinc as one of the metals. Amongst iron sulphides, types with yellowish or gold appearance are especially suitable. Most preferably the metal sulphide is zinc  
10 sulphide, such as albalith, cleiophane, maltraite, sachtolith, sphalerite or wurtzite. When the composition of the invention is brightly coloured it is preferred to use a metal sulphide which is white (such as zinc sulphide) or a metal sulphide which is a similar colour to the composition e.g. cadmium sulphide when the composition is yellow-red so that the addition of the metal sulphide does not result in any  
15 significant discolouration of the composition.

The metal sulphide is preferably of fine particle size (such as below about 50  $\mu\text{m}$ , in particular below about 20  $\mu\text{m}$ ), most preferred of pigmentary grade (such as below about 5  $\mu\text{m}$ ), such as for example C.I. Pigment Yellow 35, C.I. Pigment Yellow 37 or especially C.I. Pigment White 7.

20 The amount of the metal sulphide present in the polymeric composition is preferably sufficient to produce a dark marking on the moulded article when it has been irradiated with a laser beam at an irradiation level of 5 - 50 ampere at a frequency of 1 - 100 kHz in the range of 500 - 2100 nm. More preferably the amount of metal sulphide present in the polymeric composition ranges from 0.05 to 3  
25 percent by weight, based on the total weight of the composition. Even more preferably the metal sulphide is present in an amount of from 1.0 to 2.5 percent by weight, based on the total weight of the composition.

Additional pigments, dyes and/or inert fillers may be added to the polymeric composition of the invention depending on the desired colour. The kinds and

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amounts of these additives are decided appropriately in accordance with the end use. In particularly preferred compositions pigments are used so that a product moulded using the composition would be pink, red, yellow, orange, lime green, lilac, mid to light blue or turquoise in colour. The pigments are preferably non-black  
5 organic or inorganic pigments. The pigments are best present in an amount of from 0.01 to 10.0 percent by weight, based on the total weight of the composition.

Further additives may be incorporated into the composition to improve the moulding properties of the resin or environmental adaptability of the resulting moulded articles. Useful additives include antioxidants, antistatic agents, light stabilizers, UV  
10 absorbers, neutralizing agents, rust inhibitors, lubricants, flame retardants, nucleating agents, dispersants, processing stabilizers, flow improvers, and the like. The kinds and amounts of these additives are well-known to the skilled artisan who decides appropriately in accordance with the intended end use.

The polymeric composition of the present invention may be prepared by  
15 compounding the above-described polymeric material, metal sulphide and mica or micaceous material and, if desired, further additives. The compounding method is not limited, and any known technique can be adopted. Preferably the method is carried out either by intensive shear Z blade mixing or by extrusion (single screw or twin screw counter or co-rotating). But it is also possible just to mix or blend the  
20 components, especially if sufficient homogenization is ensured during the subsequent processing step.

The method for forming an article out of the composition is not particularly restricted. Products can be produced for example by an extrusion process, by moulding or any other similar process as known in the art. Compression moulding,  
25 injection moulding and blow moulding processes are particularly applicable. The effects of the present invention are noticeably manifested when the polymeric composition is injection moulded because the resulting injection moulded articles are excellent in surface appearance such as gloss and uniformity.

The invention is in particular directed to livestock ear tags, but is in no way limited

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to such articles. Excellent results are also obtained on other articles, such as automotive parts, bottles or bottle caps, tubes, pipes, containers, covers, keyboards, labels, chips, security documents such as identity or credit cards, office, household, school and military articles, toys, and many more which the skilled  
5 artisan will obviously recognize. Laser marking may be used to identify, personalize, decorate, follow up or deface such articles. The marks may, for example, contain information about the article itself, its contents, price, dimensions, purpose, date of manufacture or durability, holder, owner, manufacturer, distributor or country of origin.

10 The resulting article can readily be marked with letters, digits, patterns, barcodes, pointcodes, symbols, drawings etc. by scanning it with a continuous or discontinuous laser beam. Lasers used for marking are not limited and include gas lasers, such as a carbon dioxide laser, an excimer laser, and an argon laser, and solid lasers, such as a ruby laser, a semiconductor laser, and a YAG laser. One  
15 preferred laser used is a Nd:YAG laser operating at a wavelength of either 532 nm or 1064 nm. In one embodiment the product is marked by using a Nd:YAG laser at a pulse frequency of 6200 Hz; a scanning speed of 1600 mm/sec and a laser power of 26.5 A.

20 It should be noted that because the polymeric material itself shows little absorption at the wavelength of laser irradiation, the laser marking does not significantly affect the practical performance of the moulded article.

The present invention will now be described in greater detail with reference to the following examples, but it should be understood that the present invention should not be construed as being limited thereto. Unless otherwise noted, all the referen-  
25 ces to percentage are by weight based on the total weight of the composition.

Example 1: The following ingredients are blended together:

CAS No. 13463-67-7 (C.I. Pigment White 6 = TiO <sub>2</sub> )	2.02%
CAS No. 471-34-1 (calcium carbonate)	1.5%
CAS No 112945-52-5 (fumed synthetic amorphous silica)	0.205%

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	CAS No. 154946-66-4 (C.I. Pigment Yellow 191:1)	0.195%
	CAS No. 5590-18-1 (C.I. Pigment Yellow 110)	0.096%
	Mecon™ MP 105	0.075%
	Iriodin™ LS825 (surface treated mica)	0.3%
5	CAS No. 1314-98-3 (zinc sulphide)	1.7%
	Elastollan™ WY01388 (polyurethane resin)	92.759%
	CAS No. 2440-22-4 (Tinuvin® P, Ciba Spec. Chem. Inc.)	0.5%
	CAS No. 65447-77-0 (Chimassorb® 622LD, Ciba Spec. Chem.)	0.5%
	CAS No. 6683-19-8 (Irganox® 1010, Ciba Spec. Chem. Inc.)	0.15%
10	<u>Example 2:</u> The following ingredients are blended together:	
	Iriodin™ LS820 (surface treated mica)	0.3%
	MC50™ (melamine cyanurate)	1.0%
	Zinc sulphide	1.0%
	TU20464 Yellow (masterbatch)	2.0%
15	CAS No. 2440-22-4 (Tinuvin® P, Ciba Spec. Chem. Inc.)	0.5%
	CAS No. 65447-77-0 (Chimassorb® 622LD, Ciba Spec. Chem.)	0.5%
	CAS No. 6683-19-8 (Irganox® 1010, Ciba Spec. Chem. Inc.)	0.15%
	CAS No. 471-34-1 (calcium carbonate)	1.5%
	CAS No 112945-52-5 (fumed synthetic amorphous silica)	0.075%
20	Wax mix (5% Cabosil™ M5, 40% calcium stearate, 55% LDPE wax)	0.1%
	Thermoplastic polyurethane resin	92.875%

Example 3: The following ingredients are blended together:

	Iriodin™ LS825 (surface treated mica)	0.3%
	FT-3000™ (metal oxide)	1.0%
25	Zinc sulphide	1.0%
	TU20464 Yellow (masterbatch)	2.0%
	CAS No. 2440-22-4 (Tinuvin® P, Ciba Spec. Chem. Inc.)	0.5%
	CAS No. 65447-77-0 (Chimassorb® 622LD, Ciba Spec. Chem.)	0.5%
	CAS No. 6683-19-8 (Irganox® 1010, Ciba Spec. Chem. Inc.)	0.15%
30	CAS No. 471-34-1 (calcium carbonate)	1.5%



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CAS No 112945-52-5 (fumed synthetic amorphous silica)	0.075%
Wax mix (as above)	0.1%
Thermoplastic polyurethane resin	92.875%

**Example 4:** The following ingredients are blended together:

5	Iriodin LS820 (surface treated mica)	0.3%
	FT-3000™ (metal oxide)	1.0%
	Zinc sulphide	1.0%
	TU20464 Yellow (masterbatch)	2.0%
	CAS No. 2440-22-4 (Tinuvin® P, Ciba Spec. Chem. Inc.)	0.5%
10	CAS No. 65447-77-0 (Chimassorb® 622LD, Ciba Spec. Chem.)	0.5%
	CAS No. 6683-19-8 (Irganox® 1010, Ciba Spec. Chem. Inc.)	0.15%
	CAS No. 471-34-1 (calcium carbonate)	1.5%
	CAS No 112945-52-5 (fumed synthetic amorphous silica)	0.075%
	Wax mix (as above)	0.1%
15	Thermoplastic polyurethane resin	92.875%

In the abovementioned descriptions in each case where a "CAS" number is recited it is the Chemical Abstracts Service registry number (the details can be obtained on [www.nicnas.gov.au/obligations/aics/search.asp](http://www.nicnas.gov.au/obligations/aics/search.asp)). "C.I." refers to the Colour Index International edited by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists ([www.colour-index.org](http://www.colour-index.org)).

Mecon™ MP 105 is a product of PolyOne Denmark and is an ethylene co-polymer alkyd compatibiliser. Iriodin™ LS820 and LS825 are products of Merck, Inc. and are both treated micas which have greater than 50% mica and are surface treated with metal oxides. Elastollan™ WY01388 is a thermoplastic polyurethane resin of BASF. FT-3000™ is a product of Ishihara Sangyo Kaisha Ltd and is TiO<sub>2</sub> and Sb<sub>2</sub>O<sub>5</sub> doped with tin oxide. TU20464 Yellow is a yellow/orange thermoplastic masterbatch from Ciba Spec. Chem. Pty. Inc. containing compatibilisers and wax.

In each case these materials were compounded in a Z blade mixer at 190°C for approximately 20 seconds after flux. The respective samples were then

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compression moulded at 200°C for 2-3 minutes at 1379 kPa [200 psi] and then cooled. Subsequently, the platelets were mounted and laser marked using a Nd:YAG laser operating at a wavelength of 1064 nm.

In each of examples 1 to 4, the resulting laser marking exhibited excellent definition. A barcode marked on the products could be visibly read using a barcode scanner using a red laser. Successful markings were possible over a wide range of different colours. The invention described in this specification is applicable when using pigmented polymeric materials of various different colours. Preferably the metal sulphide used is either the same or similar to the colour of the intended product or is white such as in the case of zinc sulphide.

Utilising appropriate pigments, the applicants have utilised the compositions of the invention to produce moulded products having the following colours and associated values of lightness and chroma (C.I.E. 1976 L\*C\*h colour space).

Colour	Lightness L*	Chroma C*
Off white	88.89	2.47
Yellow	91.02	55.41
Yellow orange	77.27	65.84
Red orange	61.12	61.5
Orange	73.86	57.38
Light pink	65.42	45.73
Pink	65.58	41.39
Red	49.14	53.58
Pale turquoise	76.27	17.05

It will be appreciated that these values of lightness and chroma for various colours are values that might be typically expected using the compositions and processes of the invention. Best results are obtained with colours having a lightness L\* of from

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about 40 to 100, preferably from 50 to 98, most preferred from 60 to 95. However, the invention is not at all restricted to such colours or lightness or chroma values.

In general, it will be desired that the marked areas be as dark as possible, with a lightness  $L^*$  and chroma  $C^*$  each from 0 to 20, preferably from 0 to 10. However, it is not necessary that this goal is always achieved. A decrease in lightness  $L^*$  of at least about 5, preferably at least 10, most preferred at least 20, is easily noticeable even by people not used to evaluating colours and amply sufficient in most cases.

The laser marked moulded articles of the invention may be used for any application in which it is necessary for such indicia to be visible. By way of example it is contemplated that the polymeric compositions could be compounded to form a livestock product such as an ear tag and subsequently marked using laser processing to enable livestock handlers to track and readily identify stock.

Throughout the description and claims of this specification, use of the word "comprise" and variations of the word, such as "comprising" and "comprises", is not intended to exclude any other additives, components, integers or steps.

While the invention has been described in detail and with reference to specific examples, it will be apparent to one skilled in the art that various changes and modifications can be made without departing from the spirit and scope of the invention as defined in the following claims.